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(54) CATALYST FOR POLYMERIZING CYCLIC OLEFINS AND PRODUCTION OF CYCLIC OLEFIN POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a cyclic olefin polymerization catalyst capable of realizing a high cyclic olefin conversion in an extremely small amount, and to provided a method for producing a high mol.wt. cyclic olefin polymer.

SOLUTION: This catalyst for polymerizing a cyclic olefin comprises (A) a transition metal compound, (B) a compound capable of reacting with the transition metal compound to form an ionic complex, and (C) water or an acid. A method for producing the cyclic olefinic polymer comprises polymerizing a cyclic olefin in the presence of the catalyst. This method for producing the cyclic olefinic polymer comprises polymerizing the cyclic olefin in the presence of a catalyst comprising (A) the transition metal compound and (B) the compound capable of reacting with the transition metal component to form the ionic complex in water as a dispersing medium.

JP,10-130311 Machine Translation

[Claim(s)]

[Claim 1](A) A transition metal compound, a compound which reacts to the (B) transition metal compound and forms a complex of ionicity, and a catalyst for a cyclic olefin polymerization containing (C) water.

[Claim 2](A) A transition metal compound, a compound which reacts to the (B) transition metal compound and forms a complex of ionicity, and a catalyst for a cyclic olefin polymerization containing (C) acid.

[Claim 3]The catalyst for a cyclic olefin polymerization according to claim 2, wherein acid (C) is Brønsted acid.

[Claim 4]The catalyst for a cyclic olefin polymerization according to claim 3, wherein Brønsted acid is inorganic acid.

[Claim 5]The catalyst for a cyclic olefin polymerization according to claim 3, wherein Brønsted acid is heteropoly acid or its hydrate.

[Claim 6]The catalyst for a cyclic olefin polymerization according to claim 3, wherein Brønsted acid is a carboxylic acid compound.

[Claim 7]The catalyst for a cyclic olefin polymerization according to claim 3, wherein Brønsted acid is phenol or phenols.

[Claim 8]The catalyst for a cyclic olefin polymerization according to any one of claims 1 to 7, wherein a transition metal compound (A) is the 10th group transition metal compound.

[Claim 9]The catalyst for a cyclic olefin polymerization according to any one of claims 1 to 7, wherein a transition metal compound (A) is a palladium compound.

[Claim 10]The catalyst for a cyclic olefin polymerization according to any one of claims 1 to 9, wherein a compound (B) which reacts to a transition metal compound and forms a complex of ionicity is a compound which generates an anion of non-ligating property by a reaction with a transition metal compound.

[Claim 11]The catalyst for a cyclic olefin polymerization according to any one of claims 1 to 9, wherein compounds (B) which react to a transition metal compound and form a complex of ionicity are the following (B1) - (B3) either.

(B1) Boron compound (B3) general formula $(L-H)^+$ expressed with boron compound (B-2) general formula $G^+(BQ^1Q^2Q^3Q^4)^-$ expressed with general formula $BQ^1Q^2Q^3$. $(BQ^1Q^2Q^3Q^4)$ A boron compound expressed with $^-$ (among a formula) B is a boron atom of a trivalent valence state, and $Q^1 - Q^4$ A halogen atom, A hydrocarbon group containing 1-20 carbon atoms, a halogenated hydrocarbon group containing 1-20 carbon atoms, It is 2 substituted amino groups containing a substitution silyl group containing 1-20 carbon atoms, an alkoxy group containing 1-20 carbon atoms, or 2-40 carbon atoms, and they may be the same or may differ. G^+ is a cationic acid-ized agent which can oxidize and can use a transition metal as a cation, or a cation which can draw out a ligand from a transition metal compound. L is a neutral Lewis base and $(L-H)^+$ is Brønsted acid.

[Claim 12]A manufacturing method of a cyclic olefin system polymer polymerizing in cyclic olefin using the catalyst according to any one of claims 1 to 11.

[Claim 13](A) A manufacturing method of a cyclic olefin system polymer polymerizing in cyclic olefin by using water as a dispersing solvent using a catalyst containing a transition metal compound and a compound which reacts to the (B) transition metal compound and forms a

complex of ionicity.

[Translation done.]

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of the catalyst for a cyclic olefin polymerization, and a cyclic olefin system polymer.

[0002]

[Description of the Prior Art] The cyclic olefin represented by norbornene polymerizes by various kinds of polymerizing methods, and giving the cyclic olefin system polymer which makes addition structure a subject is known. Generally such a cyclic olefin system polymer has a high glass transition temperature as compared with the un-annular olefin system polymer. The application as a film or various mold goods is expected as high-heat-resistance resin.

[0003] Various kinds of things are known as a manufacturing method of this cyclic olefin system polymer. For example, about the norbornene system polymer, the method of using $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ for a U.S. Pat. No. 3330815 specification at a catalyst is proposed. The method of using for JP,4-63807,A the catalyst which consists of a transition metal compound ingredient and an aluminosilicate ingredient is proposed. However, there was a problem that catalytic activity was low in the former, in order to have to use a lot of aluminosilicate for the latter, a lot of metal remained in the polymer, and there was a problem of becoming causes, such as degradation of a polymer and coloring.

[0004] The method of manufacturing the cyclic olefin system polymer containing a copolymer is proposed using the catalyst which consists of a compound ingredient which reacts to a transition metal compound ingredient and a transition metal compound at JP,5-262821,A, and forms the complex of ionicity. Although this method is a method excellent in the point that comparatively high catalyst efficiency can be attained, without using co-catalysts, such as aluminosilicate, so much, When it is the point that the inversion rate of cyclic olefin is low, and many, still, the point which needs use of the difficult organoaluminum compound of handling as a co-catalyst is not enough.

[0005] The manufacturing method of the cyclic olefin system polymer using the catalyst which uses as the main ingredients the compound which reacts to a palladium compound and a transition metal compound at JP,7-304834,A, and forms the complex of ionicity as a method by which this problem has been improved is proposed. Although this method was excellent as a method which may polymerize in a high inversion rate in cyclic olefin, industrial still higher catalytic activity and improvement in the molecular weight of polymer obtained were desired.

[0006] On the other hand, research which adds water to the polymerization system of the cyclic olefin using a transition metal compound is done until now, For example, in Macromol.Symp.89,433 (1995). $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4]$ In the polymerization of the norbornene which makes $[\text{BF}_4]^-$ a catalyst, even if it adds water, it is proved that a polymer is obtained, but both polymerization activity and the molecular weight of a polymer obtained are falling compared with an additive-free system. Thus, the actual condition is not having found the satisfactory method at present still industrially about a cyclic olefin system polymer.

[0007]

[Problem(s) to be Solved by the Invention] This invention is made in light of the above-mentioned circumstances. That is, there is a technical problem of this invention in providing the method of manufacturing the catalyst for a cyclic olefin polymerization which realizes the inversion rate of high cyclic olefin with very a small amount of catalysts, and the cyclic olefin system polymer of the amount of polymers.

[0008]

[Means for Solving the Problem] As a result of repeating examination wholeheartedly that an aforementioned problem should be solved, this invention persons find out a catalyst which added water or acid to a specific catalyst system as one ingredient further, and came to complete this invention. Namely, a compound which this invention reacts to the (A) transition metal compound and the (B) transition metal compound, and forms a complex of ionicity, And a manufacturing method of a cyclic olefin system polymer which polymerizes in cyclic olefin using a catalyst for a cyclic olefin polymerization containing (C) water or acid and this catalyst is started. Furthermore, this invention starts a manufacturing method of a cyclic olefin system polymer which polymerizes in cyclic olefin by using water as a dispersing solvent using a catalyst containing the (A) transition metal compound and a compound which reacts to the (B) transition metal compound and forms a complex of ionicity.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained in detail.

(1) The cyclic olefin used in cyclic olefin this invention is the compounds in which four or more carbon atoms which may have various kinds of substituents form a ring, and include one carbon-carbon double bond in this ring. As such cyclic olefin, cyclobutene, cyclopentene, Monocycle-like olefins, such as a cyclohexene; 3-methylcyclopentene, Substitution monocycle-like olefins, such as 3-methylcyclohexene; substitution many cyclic olefin, such as multi-cyclic olefin; 1-methyl norbornene, such as norbornene and a 1 and 2-dihydrodicyclopentadiene, and 5-methyl norbornene, is illustrated.

[0010] Cyclic olefin desirable in these is the compounds expressed with following general formula [I].

(Among a formula, $R^1 - R^{12}$ may show the substituent chosen from the group which consists of a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, and an organic group with 1-20 carbon atoms independently, respectively, and R^5 , R^6 and R^7 , and R^8 may form a ring.) n shows zero or more integers.

[0011] Here as an example of an organic group with 1-20 carbon atoms which are the members of a substituent A methyl group, Alkyl groups, such as an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group, and dodecyl; A phenyl group, Aalkyl groups, such as aryl group; benzyls, such as a tolyl group and a naphthyl group, and a phenethyl group; A methylidene group, Alkylidene groups, such as an ethylidene group; Alkenyl group; methoxy groups, such as a vinyl group and an allyl group, alkoxy group [, such as an ethoxy basis,]; --

aryloxy group [, such as a phenoxy group,]; -- acyl group [, such as an acetyl group,]; -- a methoxycarbonyl group. alkoxycarbonyl group [, such as an ethoxycarbonyl group,]; -- acyloxy group [, such as an acetyloxy group,]; -- silyl group [, such as a trimethylsilyl group,] (substitution); -- a dimethylamino group. alkylamino group [, such as a diethylamino group,]; -- carboxyl group; -- cyano group; and the above-mentioned alkyl group. Some hydrogen atoms of an aryl group and an ARARU keel group can mention the basis replaced by a halogen atom, a hydroxyl group, an amino group, the acyl group, the carboxyl group, the alkoxy group, the alkoxycarbonyl group, the acyloxy group, the silyl group (substitution), the alkylamino group, or the cyano group.

[0012]A desirable substituent An alkyl group with a hydrogen atom and 1-20 carbon atoms, an aryl group with 6-20 carbon atoms, An aralkyl group with 7-20 carbon atoms, an alkylidene group with 1-20 carbon atoms, They are an alkenyl group with 2-20 carbon atoms, an acyl group with 1-20 carbon atoms, an alkoxycarbonyl group with 1-20 carbon atoms, an acyloxy group with 1-20 carbon atoms, and a silyl group (substitution) with 1-20 carbon atoms.

[0013]As an example of desirable cyclic olefin expressed with general formula [I], Norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-butyl norbornene, 5-phenyl norbornene, 5-benzyl norbornene, Tetracyclo dodecen, tricyclo decene, tricyclo undecene, Pentacyclo pentadecene, pentacyclo hexa decene, ethylidene norbornene, 8-methyltetracyclo dodecen, 8-ethyltetracyclo dodecen, 5-acetyl norbornene, 5-acetyloxy norbornene, 5-carbomethoxy norbornene, 5-ethoxycarbonyl norbornene, 5-methyl-5-carbomethoxy norbornene, 5-cyano norbornene, 8-carbomethoxy tetracyclo dodecen, 8-methyl-8-carbomethoxy tetracyclo dodecen, 8-cyano tetracyclo dodecen, etc. can be enumerated.

[0014]When polymerizing, these cyclic olefin is independent or they are used by plurality. They are the range which does not spoil the outstanding character which a cyclic olefin system polymer has, i.e., the range in which the rate of the cyclic olefin in a total monomer generally is not less than 10 % of the weight, and a range which is not preferably less than 50 % of the weight, Using cyclic olefin and other existing copolymeric monomers together with cyclic olefin does not interfere at all. As an example of other starting monomers, ethylene, propylene, 1-butene, Alkenyl aromatic hydrocarbon, such as alpha olefin; styrene, such as 4-methylpentene- 1, 1-hexene, and 1-octene; The methyl vinyl ether, alkyl vinyl ether [, such as ethyl vinyl ether,]; -- unsaturation halogenated hydrocarbon [, such as VCM/PVC,]; -- methyl acrylate. Unsaturated nitrile, such as alpha, such as ethyl acrylate and methyl methacrylate, and beta-unsaturated-carboxylic-acid-ester; acrylonitrile; carboxylic acid vinyl, such as vinyl acetate, etc. can be mentioned.

[0015](2) Transition metal compound (A)

The (A) ingredient in the catalyst of this invention is a transition metal compound. A transition metal compound is a compound which has an element of the 6th fellows to the 11th fellows of the periodic table (an IUPAC inorganic chemistry nomenclature revised edition, 1989) here. As an example of these 6th fellows to the 11th fellows' element, chromium, molybdenum, tungsten, manganese, iron, a ruthenium, cobalt, rhodium, nickel, palladium, platinum, copper, silver, etc. are mentioned. Especially if it is a compound which has these elements, it is not limited, but a desirable transition metal compound is the 10th group transition metal compound, and are various compounds, such as nickel, palladium, and platinum.

[0016]As the example, inorganic acid salt; nickel acetate of nickel, such as nickel chloride, nickel sulfate, and perchloric acid nickel, Organic acid salt of nickel, such as nickel oxalate; Nickel acetylacetonate, Nickel complexes, such as nickel phthalocyanine; A palladium chloride,

a palladium bromide, The inorganic acid salt of palladium, such as a palladous iodide, sulfuric acid palladium, and a palladium nitrate; Palladium acetate, Organic acid salt of palladium, such as trifluoro palladium acetate and palladium cyanide; Palladium acetylacetonate, Bis(allyl)palladium, dichloro(1,5-cyclo-octadiene) palladium, Dichlorobis (acetonitrile) palladium, dichlorobis (benzonitrile) palladium, Carbonyltris(triphenyl phosphine) palladium, dichlorobis (triethylphosphine) palladium, JIASETOBISU (triphenyl phosphine) palladium, tetrakis (triphenyl phosphine) palladium, Dichloro[1,2-bis(diphenylphosphino)ethane] palladium, bis[1,2-bis(diphenylphosphino)ethane] palladium, a tetramine palladium nitrate, Palladium complexes, such as tetrakis (acetonitrile) palladium tetrafluoroborate; platinum complexes, such as inorganic acid salt; platinum acetylacetonate of platinum, such as a platinum chloride and iodination platinum, etc. can be mentioned. The 10th group transition metal compounds desirable in these are a compound of palladium, and a compound of nickel, and the still more desirable 10th group transition metal compound is a compound of palladium. Especially a desirable transition metal compound (A) A palladium chloride, a palladium bromide, They are a palladous iodide, sulfuric acid palladium, a palladium nitrate, palladium acetate, dichlorobis (acetonitrile) palladium, dichlorobis (benzonitrile) palladium, and palladium acetylacetonate.

[0017](3) The compound (B) which reacts to a transition metal compound and forms the complex of ionicity

The (B) ingredient in the catalyst of this invention is a compound which reacts to a transition metal compound and forms the complex of ionicity. Anything can be used for it, if the compound (B) which reacts to a transition metal compound and forms the complex of ionicity reacts to a transition metal compound and the complex of ionicity can be formed. A compound (B) is a compound which generates the anion of non-ligating property by a reaction with a transition metal compound preferably.

[0018]The Lewis acid which can become a non-ligating property anion which uses a transition metal compound (B1) as a cation, and corresponds preferably, (B-2) -- general formula G^+A^- (however, the cationic acid-ized agent which G^+ can oxidize a transition metal and can be used as a cation.) Or it is a cation which can draw out a ligand from a transition metal compound, A^- is a non-ligating property anion. The compound expressed or (B3) general formula $(L-H)^+A^-$. (however, L is a neutral Lewis base, $(L-H)^+$ is Broensted acid, a transition metal can be used as a cation and A^- is a non-ligating property anion.) -- it is either of the compounds which is expressed.

[0019](B1), (B-2), and (B3) are boron compounds more preferably, respectively.

[0020]The above-mentioned Lewis acid (B1) is a general formula still more preferably. It is a boron compound expressed with $BQ^1Q^2Q^3$. B is a boron atom of a trivalent valence state, and $Q^1 - Q^3$ However, a halogen atom, The hydrocarbon group containing 1-20 carbon atoms, the halogenated hydrocarbon group containing 1-20 carbon atoms, It is 2 substituted amino groups containing the substitution silyl group containing 1-20 carbon atoms, the alkoxy group containing 1-20 carbon atoms, or 2-40 carbon atoms, and they may be the same or may differ.

[0021]As an example of Lewis acid (B1), tris(pentafluorophenyl) borane, Tris(2,3,5,6-tetrafluorophenyl) borane, tris(2,3,4,5-tetrafluorophenyl) borane, Although tris(3,4,5-trifluorophenyl) borane, tris(2,3,4-trifluorophenyl) borane, phenylbis(pentafluorophenyl)borane, etc. are mentioned, it is tris(pentafluorophenyl) borane most preferably.

[0022]The compound (B-2) expressed with above general formula G^+A^- is a boron compound expressed with general formula $G^+(BQ^1Q^2Q^3Q^4)^-$ still more preferably. However, B is a boron atom of a trivalent valence state, and $Q^1 - Q^4$ of it are the same as that of Q^1 in the above-

mentioned Lewis acid (B1) - Q^3 .

[0023]General formula As an example of a compound expressed with $G^+(BQ^1Q^2Q^3Q^4)^-$, A ferro SENIUMU cation, an alkylation ferro SENIUMU cation, a silver positive ion, etc. are mentioned to G^+ which is a cationic acid-ized agent, and a triphenylmethyl cation etc. are mentioned to G^+ which is a cation which can draw out a ligand from a transition metal compound. In $^-$ which is a non-ligating property anion ($BQ^1Q^2Q^3Q^4$). Tetrakis (pentafluorophenyl) borate, tetrakis (2,3,5,6-tetrafluoro phenyl) borate, Tetrakis (2,3,4,5-tetrafluoro phenyl) borate, Tetrakis (3,4,5-trifluorophenyl) borate, tetrakis (2, 2, 4-trifluorophenyl) borate, phenylbis(pentafluorophenyl)borate, tetrakis(3,5-bis-trifluoromethylphenyl)borate, etc. are mentioned.

[0024]As such concrete combination, ferro SENIUMU tetrakis (pentafluorophenyl) borate, 1,1-dimethylferrocenium tetrakis(pentafluorophenyl)borate, Although silver tetrakis (pentafluorophenyl) borate, triphenylmethyl tetrakis (pentafluorophenyl) borate, triphenylmethyl tetrakis(3,5-bis-trifluoromethylphenyl)borate, etc. can be mentioned, It is triphenylmethyl tetrakis (pentafluorophenyl) borate most preferably.

[0025]The compound (B3) expressed with above general formula $(L-H)^+A^-$ is a boron compound expressed with general formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$ still more preferably. However, B is a boron atom of a trivalent valence state, and $Q^1 - Q^4$ of it are the same as that of Q^1 in the above-mentioned Lewis acid (B1) - Q^3 .

[0026]As an example of a compound expressed with general formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$, In $^+$ which is Broensted acid (L-H). Trialkyl substitution ammonium, N, and N-dialkyl anilinium, dialkyl ammonium and doria -- reel phosphonium etc. are mentioned and the same thing as the above-mentioned is mentioned to $^-$ which is a non-ligating property anion ($BQ^1Q^2Q^3Q^4$).

[0027]As such concrete combination, triethyl ammonium tetrakis (pentafluorophenyl) borate, Tripropylammoniumtetrakis(pentafluorophenyl)borate, Tori (normal butyl) ammonium tetrakis (pentafluorophenyl) borate, Tori (normal butyl) ammonium tetrakis(3,5-bis-trifluoromethylphenyl)borate, N and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate, N,N-diethyl anilinium tetrakis (pentafluorophenyl) borate, N, N-2, 4, 6-pentamethylanilinium tetrakis (pentafluorophenyl) borate, N and N-dimethyl anilinium tetrakis(3,5-bis-trifluoromethylphenyl)borate, Diisopropyl ammonium tetrakis (pentafluorophenyl) borate, Dicyclohexyl ammonium tetrakis (pentafluorophenyl) borate, triphenyl phosphonium tetrakis (pentafluorophenyl) borate, Tori (methylphenyl) phosphonium tetrakis (pentafluorophenyl) borate, Although Tori (dimethylphenyl) phosphonium tetrakis (pentafluorophenyl) borate etc. can be mentioned, It is Tori (normal butyl) ammonium tetrakis (pentafluorophenyl) borate or N, and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate most preferably.

[0028](4) Water or acid (C)

The (C) ingredient in the catalyst of this invention is water or acid. It is Broensted acid preferably as acid. If Broensted acid is a compound which has the character to give a proton and is a compound which has such character here, it will not be limited in particular. As an example of acid, chloride, sulfuric acid, nitric acid, hypochlorous acid, perchloric acid, boric acid, Inorganic acid, such as phosphoric acid, permanganic acid, dichromic acid, hydrogen peroxide solution, and dim-ized hydro acid; Tungstophosphoric acid, Heteropoly acid or its hydrates, such as molybdophosphoric acid; Formic acid, acetic acid, propionic acid, Triphloroacetic acid, monochloroacetic acid, dichloroacetic acid, butanoic acid, benzoic acid, Methylbenzoic acid, chlorobenzoic acid, methoxybenzoic acid, fumaric acid, maleic acid, Carboxylic acid, such as salicylic acid and naphthalene carboxylic acid; Phenol, Phenols, such as cresol, fluorophenol,

chlorophenol, hydroquinone, bromophenol, methoxy phenol, and cyanophenol, an aminophenol, a nitrophenol, and pentafluorophenol; solid acid, such as silica and alumina, is mentioned.

[0029]Desirable Brønsted acid Chloride, perchloric acid, boric acid, hydrogen peroxide solution, They are tungstophosphoric acid, dim-ized hydro acid, formic acid, acetic acid, propionic acid, triphloroacetic acid, benzoic acid, fumaric acid, maleic acid, a glyoxal, phenol, pentafluorophenol, 4-methoxyphenol, cresol, and hydroquinone. These compounds can be independent or can be used by plurality.

[0030](5) The catalyst for a cyclic olefin polymerization of catalyst this invention for a cyclic olefin polymerization is a catalyst containing the above-mentioned (A) ingredient, the (B) ingredient, and the (C) ingredient. In a suitable solvent, may use these ingredients as a beforehand mixed solution, and the (A) ingredient, the (B) ingredient, and the (C) ingredient, for example, The (A) ingredient, the (B) ingredient and the (C) ingredient, or the solution that melted them in the monomer or the suitable solvent may be supplied to a polymerization system simultaneous or independently, and it may be made to contact within a polymerization system.

[0031]as opposed to the monomer which it cannot generally define the range since the amount of the ingredient (A) used differs in the suitable value according to the kind and other polymerization conditions of the cyclic olefin chosen, but is usually used -- 0.00001 - 1-mol % -- they are 0.0001 - 0.1-mol % preferably. Although the amount in particular of the ingredient (B) used is not restricted, either, 0.1-100 mol is usually 0.5-10 mol preferably per 1 mol of ingredients (A). Although the amount of the ingredient (C) used is not restricted, either, it is usually 0.001 mol or more per mol of ingredient (A). Although it is about 0.1-100000 mol per mol of ingredient (A) preferably, it is also possible to use it in large quantities and to use as a polymerization solvent.

[0032](6) In manufacture this invention of a cyclic olefin system polymer, although a polymerization method in particular should not be limited, For example, aliphatic hydrocarbon, such as butane, pentane, hexane, heptane, and octane, Aromatic hydrocarbon, such as benzene, toluene, and xylene, methylene dichloride, Halogenated hydrocarbon, such as ethylene dichloride, methanol, ethanol, Ether, such as alcohols, such as propanol and butanol, diethylether, and a tetrahydrofuran, Ketone, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone. The solvent polymerization which uses solution and water, such as acetic acid, chloride, and perchloric acid, for a solvent as independence or multiple mixed liquor or slurry polymerization, a vapor phase polymerization, high voltage ionic polymerization in the inside of a gaseous monomer, etc. are possible, and either a continuation polymerization or a batch process polymerization is possible.

[0033]In a solvent polymerization or slurry polymerization, although the polymerization temperature can usually take the range of -50-200 **, the range of -20-100 ** is preferred especially, and polymerization pressure has ordinary pressure - preferred 60 kg/cm²G. In a vapor phase polymerization, 1 - 30 kg/cm²G of polymerization temperature is [60-120 ** and polymerization pressure] preferred. In high voltage ionic polymerization, 300 - 2500 kg/cm²G of polymerization temperature is [150-300 ** and polymerization pressure] preferred. Although polymerization time is generally suitably determined by the kind of polymer made into the purpose, and the reaction apparatus, it can usually take the range of for [1 minute] - 20 hours. This invention can also add chain transfer agents, such as hydrogen, in order to adjust the molecular weight of a copolymer.

[Example]Although an example explains this invention concretely, this invention does not have the range hereafter limited by this example. [eta] in an example is the limiting viscosity

measured at 135 °C by using a tetralin as a solvent.

[0034] In the 300-ml round-bottom separable flask which carried out the example 1 nitrogen purge, dichlorobis (benzonitrile) palladium 0.001 millimol, 10 ml (50 millimols as norbornene) of toluene solutions of the norbornene of 100 ml of drying toluene and 5-mol % concentration and water 1mmol were taught and warmed, and it made with a 50 °C homogeneous solution. Here, triphenylmethyl tetrakis (pentafluorophenyl) borate 0.001 millimol was added here, and churning was continued for 15 minutes at 50 °C. Then, this reaction mixture was invested in 100 ml of methanol, and RO °C of the precipitating white solid was carried out. The yield of the polymer which obtained it with methanol by carrying out reduced pressure drying of this solid after washing was 288 mg (1150 kg/mol-Pd as 6.1% and catalytic activity as an inversion rate of norbornene). The absorption based on a carbon-carbon double bond was not observed in the infrared absorption spectrum of this polymer, but it was confirmed that this polymer is poly norbornene of saturation structure. $[\eta]$ of this polymer was 0.63 dl/g.

[0035] Except having changed the water in example 2 Example 1 into 40% glyoxal solution 145mul, it was operated like Example 1 and 1.44 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5760 kg/mol-Pd as catalytic activity 31%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0036] Except having changed the water in example 3 Example 1 into 1.0 mol/l. of chloride 18mul, it was operated like Example 1 and 305 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1220 kg/mol-Pd as catalytic activity 6.5%. $[\eta]$ of the polymer was 0.28 dl/g.

[0037] Except having changed the water in example 4 Example 1 into 60% perchloric acid solution 160mul, it was operated like Example 1 and 1.84 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 7350 kg/mol-Pd as catalytic activity 39%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0038] Except having changed the water in example 5 Example 1 into 31% hydrogen-peroxide-solution 18mul, it was operated like Example 1 and 338 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1350 kg/mol-Pd as catalytic activity 7.2%. $[\eta]$ of this polymer was 1.23 dl/g.

[0039] Except having changed the water in example 6 Example 1 into 42% hydro acid [dim-ized] solution 209mul, it was operated like Example 1 and 1.447 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5790 kg/mol-Pd as catalytic activity 31%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0040] Except having changed the water in example 7 Example 1 into boric acid, it was operated like Example 1 and 585 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 2320 kg/mol-Pd as catalytic activity 12%. $[\eta]$ of this polymer was 2.38 dl/g.

[0041] Except having changed water 1mmol in example 8 Example 1 into tongue strike IV phosphoric acid hydrate 0.1mmol, it was operated like Example 1 and 1.24 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 4950 kg/mol-Pd as catalytic activity 26%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0042] Except having changed water 1mmol in example 9 Example 1 into tongue strike IV

phosphoric acid hydrate 0.1mmol and water 1mmol, it was operated like Example 1 and 1.83 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 7320 kg/mol-Pd as catalytic activity 39%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0043]Except having changed the water in example 10 Example 1 into 1.0 mol/l. of acetic acid 18mul, it was operated like Example 1 and 1.25 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 4990 kg/mol-Pd as catalytic activity 27%. [eta] of this polymer was 2.33 dl/g.

[0044]Except having changed the water in example 11 Example 1 into 1.0 mol/l. of formic acid 18mul, it was operated like Example 1 and 0.398 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1590 kg/mol-Pd as catalytic activity 8.5%. [eta] of this polymer was 2.62 dl/g.

[0045]Except having changed water 1mmol in example 12 Example 1 into triphloroacetic acid 1mmol and water 1mmol, it was operated like Example 1 and 307 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1240 kg/mol-Pd as catalytic activity 6.6%. [eta] of this polymer was 0.37 dl/g.

[0046]Except having changed the water in example 13 Example 1 into phenol, it was operated like Example 1 and 276 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1100 kg/mol-Pd as catalytic activity 5.9%. [eta] of this polymer was 0.36 dl/g.

[0047]Except having changed the water in example 14 Example 1 into pentafluorophenol, it was operated like Example 1 and 175 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 700 kg/mol-Pd as catalytic activity 3.7%.

[0048]Except having changed the water in example 15 Example 1 into 4-methoxyphenol, it was operated like Example 1 and 270 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1080 kg/mol-Pd as catalytic activity 5.7%. [eta] of this polymer was 0.57 dl/g.

[0049]Except having changed the water in example 16 Example 1 into hydroquinone, it was operated like Example 1 and 436 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1740 kg/mol-Pd as catalytic activity 9.3%.

[0050]Except not having added water 1mmol in comparative example 1 Example 1, when it was operated like Example 1, 150 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 600 kg/mol-Pd as catalytic activity 3.2%. [eta] of this polymer was 0.20 dl/g.

[0051]Except having changed water 1mmol in example 17 Example 1 into water 10mmol, it was operated like Example 1 and 892 mg of poly norbornene was obtained. This yield is equivalent to % as an inversion rate of norbornene, and equivalent to 3570 kg/mol-Pd as catalytic activity. [eta] of this polymer was 1.92 dl/g.

[0052]Except having changed water 1mmol in example 18 Example 1 into water 50mmol, it was operated like Example 1 and 1.31 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5220 kg/mol-Pd as catalytic activity 28%. [eta] of this polymer was 2.74 dl/g.

[0053]Except having changed water 1mmol in example 19 Example 1 into water 100mmol, it was operated like Example 1 and 1.28 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5130 kg/mol-Pd as catalytic activity 27%. The system of reaction was presenting the slurry form to which the formed

polymer was suspended in toluene. [eta] of the 135 ** tetralin fusible part of this polymer was dl/g.

[0054]Except having changed 100 ml of drying toluene in the example 20 comparative example 1 into 100 ml of water, it was operated like the comparative example 1 and 818 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 3270 kg/mol-Pd as catalytic activity 17%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in water. It was insoluble also to toluene in this polymer.

[0055]Except having changed 1.0 mol/l. of acetic acid 18mul in example 21 Example 10 into 0.01 mol/l. of acetic acid 18mul, it was operated like Example 10 and 712 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 2850 kg/mol-Pd as catalytic activity 15%. [eta] of this polymer was 1.81 dl/g.

[0056]Except having changed 1.0 mol/l. of acetic acid 18mul in example 22 Example 10 into 0.1 mol/l. of acetic acid 18mul, it was operated like Example 10 and 1.382 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5530 kg/mol-Pd as catalytic activity 29%. [eta] of this polymer was 2.79 dl/g.

[0057]Except having changed 1.0 mol/l. of acetic acid 18mul in example 23 Example 10 into 10 mol/l. acetic acid 18mul, it was operated like Example 10 and 902 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 3610 kg/mol-Pd as catalytic activity 19%. [eta] of this polymer was 1.87 dl/g.

[0058]Except having changed churning time 15 minutes in example 24 Example 1 in 60 minutes, it was operated like Example 1 and 844 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 844 kg/mol-Pd as catalytic activity 18%. [eta] of this polymer was 0.89 dl/g.

[0059]Except having changed churning time 15 minutes in the comparative example 2 comparative example 1 in 60 minutes, it was operated like the comparative example 1 and 350 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 350 kg/mol-Pd as catalytic activity 7.5%. [eta] of this polymer was 0.55 dl/g.

[0060]In the 300-ml round-bottom separable flask which carried out the example 25 nitrogen purge, palladium acetylacetonate 0.002 millimol, 3 ml (30 millimols as norbornene) of toluene solutions of the norbornene of 27 ml of drying toluene and 5-mol [l.] concentration and water 20mmol were taught and warmed, and it made with a 50 ** homogeneous solution. Here, triphenylmethyl tetrakis (pentafluorophenyl) borate 0.002 millimol was added here, and churning was continued for 5 minutes at 50 **. This reaction mixture was invested in 100 ml of methanol, and RO ** of the precipitating white solid was carried out. The yield of the polymer which obtained it with methanol by carrying out reduced pressure drying of this solid after washing was 790 mg (4740 kg/mol-Pd as 56% and catalytic activity as an inversion rate of norbornene). The absorption based on a carbon-carbon double bond was not observed in the infrared absorption spectrum of this polymer, but it was confirmed that this polymer is poly norbornene of saturation structure. [eta] of this polymer was 3.25 dl/g.

[0061]Except not having added water 20mmol in comparative example 3 Example 25, it was operated like Example 25 and 177 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1060 kg/mol-Pd as catalytic activity 13%.

[0062]

[Effect of the Invention]As explained in full detail above, according to the method of this invention, a useful cyclic olefin system polymer can be efficiently produced using very a small

amount of catalysts, and the industrial value is size very much.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacturing method of the catalyst for a cyclic olefin polymerization, and a cyclic olefin system polymer.

PRIOR ART

[Description of the Prior Art] The cyclic olefin represented by norbornene polymerizes by various kinds of polymerizing methods, and giving the cyclic olefin system polymer which makes addition structure a subject is known. Generally such a cyclic olefin system polymer has a high glass transition temperature as compared with the un-annular olefin system polymer. The application as a film or various mold goods is expected as high-heat-resistance resin.

[0003] Various kinds of things are known as a manufacturing method of this cyclic olefin system polymer. For example, about the norbornene system polymer, the method of using $\text{Pd}(\text{C}_6\text{H}_5 \text{ CN})_2\text{Cl}_2$ for a U.S. Pat. No. 3330815 specification at a catalyst is proposed. The method of using for JP,4-63807,A the catalyst which consists of a transition metal compound ingredient and an aluminoxane ingredient is proposed. However, there was a problem that catalytic activity was low in the former, in order to have to use a lot of aluminoxane for the latter, a lot of metal remained in the polymer, and there was a problem of becoming causes, such as degradation of a polymer and coloring.

[0004] The method of manufacturing the cyclic olefin system polymer containing a copolymer is proposed using the catalyst which consists of a compound ingredient which reacts to a transition metal compound ingredient and a transition metal compound at JP,5-262821,A, and forms the complex of ionicity. Although this method is a method excellent in the point that comparatively high catalyst efficiency can be attained, without using co-catalysts, such as aluminoxane, so much, When it is the point that the inversion rate of cyclic olefin is low, and many, still, the point which needs use of the difficult organoaluminium compound of handling as a co-catalyst is not enough.

[0005] The manufacturing method of the cyclic olefin system polymer using the catalyst which uses as the main ingredients the compound which reacts to a palladium compound and a transition metal compound at JP,7-304834,A, and forms the complex of ionicity as a method by which this problem has been improved is proposed. Although this method was excellent as a method which may polymerize in a high inversion rate in cyclic olefin, industrial still higher catalytic activity and improvement in the molecular weight of polymer obtained were desired.

[0006] On the other hand, research which adds water to the polymerization system of the cyclic olefin using a transition metal compound is done until now, For example, in Macromol.Symp.89,433 (1995). $[\text{Pd}(\text{CH}_3\text{CH}_2 \text{ CN})_4]$ In the polymerization of the norbornene which makes $[\text{BF}_4]_2$ a catalyst, even if it adds water, it is proved that a polymer is obtained, but both polymerization activity and the molecular weight of a polymer obtained are falling

compared with an additive-free system. Thus, the actual condition is not having found the satisfactory method at present still industrially about a cyclic olefin system polymer.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained in full detail above, according to the method of this invention, a useful cyclic olefin system polymer can be efficiently produced using very a small amount of catalysts, and the industrial value is size very much.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made in light of the above-mentioned circumstances. That is, there is a technical problem of this invention in providing the method of manufacturing the catalyst for a cyclic olefin polymerization which realizes the inversion rate of high cyclic olefin with very a small amount of catalysts, and the cyclic olefin system polymer of the amount of polymers.

MEANS

[Means for Solving the Problem] As a result of repeating examination wholeheartedly that an aforementioned problem should be solved, this invention persons find out a catalyst which added water or acid to a specific catalyst system as one ingredient further, and came to complete this invention. Namely, a compound which this invention reacts to the (A) transition metal compound and the (B) transition metal compound, and forms a complex of ionicity, And a manufacturing method of a cyclic olefin system polymer which polymerizes in cyclic olefin using a catalyst for a cyclic olefin polymerization containing (C) water or acid and this catalyst is started.

Furthermore, this invention starts a manufacturing method of a cyclic olefin system polymer which polymerizes in cyclic olefin by using water as a dispersing solvent using a catalyst containing the (A) transition metal compound and a compound which reacts to the (B) transition metal compound and forms a complex of ionicity.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained in detail.

(1) The cyclic olefin used in cyclic olefin this invention is the compounds in which four or more carbon atoms which may have various kinds of substituents form a ring, and include one carbon-carbon double bond in this ring. As such cyclic olefin, cyclobutene, cyclopentene, Monocycle-like olefins, such as a cyclohexene; 3-methylcyclopentene, Substitution monocycle-like olefins, such as 3-methylcyclohexene; substitution many cyclic olefin, such as multi-cyclic olefin; 1-methyl norbornene, such as norbornene and a 1 and 2-dihydrodicyclopentadiene, and 5-methyl norbornene, is illustrated.

[0010] Cyclic olefin desirable in these is the compounds expressed with following general formula [I].

(Among a formula, $R^1 - R^{12}$ may show the substituent chosen from the group which consists of a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, and an organic group with 1-20 carbon atoms independently, respectively, and R^5 , R^6 and R^7 , and R^8 may form a ring.) n shows zero or more integers.

[0011] Here as an example of an organic group with 1-20 carbon atoms which are the members of a substituent A methyl group, Alkyl groups, such as an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group, and dodecyl; A phenyl group, Aralkyl groups, such as aryl group; benzyls, such as a tolyl group and a naphthyl group, and a phenethyl group; A methylenedioxy group, Alkylidene groups, such as an ethylidene group; Alkenyl group; methoxy groups, such as a vinyl group and an allyl group, alkoxy group [, such as an ethoxy basis,]; -- aryloxy group [, such as a phenoxy group,]; -- acyl group [, such as an acetyl group,]; -- a methoxycarbonyl group. alkoxy carbonyl group [, such as an ethoxycarbonyl group,]; -- acyloxy group [, such as an acetyloxy group,]; -- silyl group [, such as a trimethylsilyl group,] (substitution); -- a dimethylamino group. alkylamino group [, such as a diethylamino group,]; -- carboxyl group; -- cyano group; and the above-mentioned alkyl group. Some hydrogen atoms of an aryl group and an ARARU keel group can mention the basis replaced by a halogen atom, a hydroxyl group, an amino group, the acyl group, the carboxyl group, the alkoxy group, the alkoxy carbonyl group, the acyloxy group, the silyl group (substitution), the alkylamino group, or the cyano group.

[0012] A desirable substituent An alkyl group with a hydrogen atom and 1-20 carbon atoms, an aryl group with 6-20 carbon atoms, An aralkyl group with 7-20 carbon atoms, an alkylidene group with 1-20 carbon atoms, They are an alkenyl group with 2-20 carbon atoms, an acyl group with 1-20 carbon atoms, an alkoxy carbonyl group with 1-20 carbon atoms, an acyloxy group with 1-20 carbon atoms, and a silyl group (substitution) with 1-20 carbon atoms.

[0013] As an example of desirable cyclic olefin expressed with general formula [I], Norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-butyl norbornene, 5-phenyl norbornene, 5-benzyl norbornene, Tetracyclo dodecen, tricyclo decene, tricyclo undecene, Pentacyclo pentadecene, pentacyclo hexa decene, ethylidene norbornene, 8-methyltetracyclo dodecen, 8-ethyltetracyclo dodecen, 5-acetyl norbornene, 5-acetyloxy norbornene, 5-carbomethoxy norbornene, 5-ethoxycarbonyl norbornene, 5-methyl-5-carbomethoxy norbornene, 5-cyano norbornene, 8-carbomethoxy tetracyclo dodecen, 8-methyl-8-carbomethoxy tetracyclo dodecen, 8-cyano tetracyclo dodecen, etc. can be enumerated.

[0014] When polymerizing, these cyclic olefin is independent or they are used by plurality. They are the range which does not spoil the outstanding character which a cyclic olefin system polymer has, i.e., the range in which the rate of the cyclic olefin in a total monomer generally is not less than 10 % of the weight, and a range which is not preferably less than 50 % of the weight, Using cyclic olefin and other existing copolymeric monomers together with cyclic olefin does not interfere at all. As an example of other starting monomers, ethylene, propylene, 1-

butene, Alkenyl aromatic hydrocarbon, such as alpha olefin; styrene, such as 4-methylpentene- 1, 1-hexene, and 1-octene; The methyl vinyl ether, alkyl vinyl ether [, such as ethyl vinyl ether,]; -- unsaturation halogenated hydrocarbon [, such as VCM/PVC,]; -- methyl acrylate. Unsaturated nitrile, such as alpha, such as ethyl acrylate and methyl methacrylate, and beta-unsaturated-carboxylic-acid-ester; acrylonitrile; carboxylic acid vinyl, such as vinyl acetate, etc. can be mentioned.

[0015](2) Transition metal compound (A)

The (A) ingredient in the catalyst of this invention is a transition metal compound. A transition metal compound is a compound which has an element of the 6th fellows to the 11th fellows of the periodic table (an IUPAC inorganic chemistry nomenclature revised edition, 1989) here. As an example of these 6th fellows to the 11th fellows' element, chromium, molybdenum, tungsten, manganese, iron, a ruthenium, cobalt, rhodium, nickel, palladium, platinum, copper, silver, etc. are mentioned. Especially if it is a compound which has these elements, it is not limited, but a desirable transition metal compound is the 10th group transition metal compound, and are various compounds, such as nickel, palladium, and platinum.

[0016]As the example, inorganic acid salt; nickel acetate of nickel, such as nickel chloride, nickel sulfate, and perchloric acid nickel, Organic acid salt of nickel, such as nickel oxalate; Nickel acetylacetonate, Nickel complexes, such as nickel phthalocyanine; A palladium chloride, a palladium bromide, The inorganic acid salt of palladium, such as a palladous iodide, sulfuric acid palladium, and a palladium nitrate; Palladium acetate, Organic acid salt of palladium, such as trifluoro palladium acetate and palladium cyanide; Palladium acetylacetonate, Bis(allyl)palladium, dichloro(1,5-cyclo-octadiene) palladium, Dichlorobis (acetonitrile) palladium, dichlorobis (benzonitrile) palladium, Carbonyltris(triphenyl phosphine) palladium, dichlorobis (triethylphosphine) palladium, JIASETOBISU (triphenyl phosphine) palladium, tetrakis (triphenyl phosphine) palladium, Dichloro[1,2-bis(diphenylphosphino)ethane] palladium, bis[1,2-bis(diphenylphosphino)ethane] palladium, a tetramine palladium nitrate, Palladium complexes, such as tetrakis (acetonitrile) palladium tetrafluoroborate; platinum complexes, such as inorganic acid salt; platinum acetylacetonate of platinum, such as a platinum chloride and iodination platinum, etc. can be mentioned. The 10th group transition metal compounds desirable in these are a compound of palladium, and a compound of nickel, and the still more desirable 10th group transition metal compound is a compound of palladium. Especially a desirable transition metal compound (A) A palladium chloride, a palladium bromide, They are a palladous iodide, sulfuric acid palladium, a palladium nitrate, palladium acetate, dichlorobis (acetonitrile) palladium, dichlorobis (benzonitrile) palladium, and palladium acetylacetonate.

[0017](3) The compound (B) which reacts to a transition metal compound and forms the complex of ionicity

The (B) ingredient in the catalyst of this invention is a compound which reacts to a transition metal compound and forms the complex of ionicity. Anything can be used for it, if the compound (B) which reacts to a transition metal compound and forms the complex of ionicity reacts to a transition metal compound and the complex of ionicity can be formed. A compound (B) is a compound which generates the anion of non-ligating property by a reaction with a transition metal compound preferably.

[0018]The Lewis acid which can become a non-ligating property anion which uses a transition metal compound (B1) as a cation, and corresponds preferably, (B-2) -- general formula G^+A^- (however, the cationic acid-ized agent which G^+ can oxidize a transition metal and can be used as a cation.) Or it is a cation which can draw out a ligand from a transition metal compound, A^- is a

non-ligating property anion. The compound expressed or (B3) general formula $(L-H)^+A^-$. (however, L is a neutral Lewis base, $(L-H)^+$ is Broensted acid, a transition metal can be used as a cation and A^- is a non-ligating property anion.) -- it is either of the compounds which is expressed.

[0019](B1), (B-2), and (B3) are boron compounds more preferably, respectively.

[0020]The above-mentioned Lewis acid (B1) is a general formula still more preferably. It is a boron compound expressed with $BQ^1Q^2Q^3$. B is a boron atom of a trivalent valence state, and $Q^1 - Q^3$ However, a halogen atom, The hydrocarbon group containing 1-20 carbon atoms, the halogenated hydrocarbon group containing 1-20 carbon atoms, It is 2 substituted amino groups containing the substitution silyl group containing 1-20 carbon atoms, the alkoxy group containing 1-20 carbon atoms, or 2-40 carbon atoms, and they may be the same or may differ.

[0021]As an example of Lewis acid (B1), tris(pentafluorophenyl) borane, Tris(2,3,5,6-tetrafluorophenyl) borane, tris(2,3,4,5-tetrafluorophenyl) borane, Although tris(3,4,5-trifluorophenyl) borane, tris(2,3,4-trifluorophenyl) borane, phenylbis(pentafluorophenyl)borane, etc. are mentioned, it is tris(pentafluorophenyl) borane most preferably.

[0022]The compound (B-2) expressed with above general formula G^+A^- is a boron compound expressed with general formula $G^+(BQ^1Q^2Q^3Q^4)^-$ still more preferably. However, B is a boron atom of a trivalent valence state, and $Q^1 - Q^4$ of it are the same as that of Q^1 in the above-mentioned Lewis acid (B1) - Q^3 .

[0023]General formula As an example of a compound expressed with $G^+(BQ^1Q^2Q^3Q^4)^-$, A ferro SENIUMU cation, an alkylation ferro SENIUMU cation, a silver positive ion, etc. are mentioned to G^+ which is a cationic acid-ized agent, and a triphenylmethyl cation etc. are mentioned to G^+ which is a cation which can draw out a ligand from a transition metal compound. In $^-$ which is a non-ligating property anion ($BQ^1Q^2Q^3Q^4$). Tetrakis (pentafluorophenyl) borate, tetrakis (2,3,5,6-tetrafluorophenyl) borate, Tetrakis (2,3,4,5-tetrafluorophenyl) borate, Tetrakis (3,4,5-trifluorophenyl) borate, tetrakis (2, 2, 4-trifluorophenyl) borate, phenylbis(pentafluorophenyl)borate, tetrakis(3,5-bis-trifluoromethylphenyl)borate, etc. are mentioned.

[0024]As such concrete combination, ferro SENIUMU tetrakis (pentafluorophenyl) borate, 1,1'-dimethylferrocenium tetrakis(pentafluorophenyl)borate, Although silver tetrakis (pentafluorophenyl) borate, triphenylmethyl tetrakis (pentafluorophenyl) borate, triphenylmethyl tetrakis(3,5-bis-trifluoromethylphenyl)borate, etc. can be mentioned, It is triphenylmethyl tetrakis (pentafluorophenyl) borate most preferably.

[0025]The compound (B3) expressed with above general formula $(L-H)^+A^-$ is a boron compound expressed with general formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$ still more preferably. However, B is a boron atom of a trivalent valence state, and $Q^1 - Q^4$ of it are the same as that of Q^1 in the above-mentioned Lewis acid (B1) - Q^3 .

[0026]As an example of a compound expressed with general formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$, In $^+$ which is Broensted acid (L-H). Trialkyl substitution ammonium, N, and N-dialkyl anilinium, dialkyl ammonium and doria -- reel phosphonium etc. are mentioned and the same thing as the above-mentioned is mentioned to $^-$ which is a non-ligating property anion ($BQ^1Q^2Q^3Q^4$).

[0027]As such concrete combination, triethyl ammonium tetrakis (pentafluorophenyl) borate, Tripropylammoniumtetrakis(pentafluorophenyl)borate, Tori (normal butyl) ammonium tetrakis (pentafluorophenyl) borate, Tori (normal butyl) ammonium tetrakis(3,5-bis-trifluoromethylphenyl)borate, N and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate, N,N-diethyl anilinium tetrakis (pentafluorophenyl) borate, N, N-2, 4, 6-pentamethylanilinium

tetrakis (pentafluorophenyl) borate, N and N-dimethyl anilinium tetrakis(3,5-bis-trifluoromethylphenyl)borate, Diisopropyl ammonium tetrakis (pentafluorophenyl) borate, Dicyclohexyl ammonium tetrakis (pentafluorophenyl) borate, triphenyl phosphonium tetrakis (pentafluorophenyl) borate, Tri (methylphenyl) phosphonium tetrakis (pentafluorophenyl) borate, Although Tri (dimethylphenyl) phosphonium tetrakis (pentafluorophenyl) borate etc. can be mentioned, It is Tri (normal butyl) ammonium tetrakis (pentafluorophenyl) borate or N, and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate most preferably.

[0028](4) Water or acid (C)

The (C) ingredient in the catalyst of this invention is water or acid. It is Brønsted acid preferably as acid. If Brønsted acid is a compound which has the character to give a proton and is a compound which has such character here, it will not be limited in particular. As an example of acid, chloride, sulfuric acid, nitric acid, hypochlorous acid, perchloric acid, boric acid, Inorganic acid, such as phosphoric acid, permanganic acid, dichromic acid, hydrogen peroxide solution, and dim-ized hydro acid; Tungstophosphoric acid, Heteropoly acid or its hydrates, such as molybdophosphoric acid; Formic acid, acetic acid, propionic acid, Triphloroacetic acid, monochloroacetic acid, dichloroacetic acid, butanoic acid, benzoic acid, Methylbenzoic acid, chlorobenzoic acid, methoxybenzoic acid, fumaric acid, maleic acid, Carboxylic acid, such as salicylic acid and naphthalene carboxylic acid; Phenol, Phenols, such as cresol, fluorophenol, chlorophenol, hydroquinone, bromophenol, methoxy phenol, and cyanophenol, an aminophenol, a nitrophenol, and pentafluorophenol; solid acid, such as silica and alumina, is mentioned.

[0029]Desirable Brønsted acid Chloride, perchloric acid, boric acid, hydrogen peroxide solution, They are tungstophosphoric acid, dim-ized hydro acid, formic acid, acetic acid, propionic acid, triphloroacetic acid, benzoic acid, fumaric acid, maleic acid, a glyoxal, phenol, pentafluorophenol, 4-methoxyphenol, cresol, and hydroquinone. These compounds can be independent or can be used by plurality.

[0030](5) The catalyst for a cyclic olefin polymerization of catalyst this invention for a cyclic olefin polymerization is a catalyst containing the above-mentioned (A) ingredient, the (B) ingredient, and the (C) ingredient. In a suitable solvent, may use these ingredients as a beforehand mixed solution, and the (A) ingredient, the (B) ingredient, and the (C) ingredient, for example, The (A) ingredient, the (B) ingredient and the (C) ingredient, or the solution that melted them in the monomer or the suitable solvent may be supplied to a polymerization system simultaneous or independently, and it may be made to contact within a polymerization system.

[0031]as opposed to the monomer which it cannot generally define the range since the amount of the ingredient (A) used differs in the suitable value according to the kind and other polymerization conditions of the cyclic olefin chosen, but is usually used -- 0.00001 - 1-mol % -- they are 0.0001 - 0.1-mol % preferably. Although the amount in particular of the ingredient (B) used is not restricted, either, 0.1-100 mol is usually 0.5-10 mol preferably per 1 mol of ingredients (A). Although the amount of the ingredient (C) used is not restricted, either, it is usually 0.001 mol or more per mol of ingredient (A). Although it is about 0.1-100000 mol per mol of ingredient (A) preferably, it is also possible to use it in large quantities and to use as a polymerization solvent.

[0032](6) In manufacture this invention of a cyclic olefin system polymer, although a polymerization method in particular should not be limited, For example, aliphatic hydrocarbon, such as butane, pentane, hexane, heptane, and octane, Aromatic hydrocarbon, such as benzene, toluene, and xylene, methylene dichloride, Halogenated hydrocarbon, such as ethylene dichloride, methanol, ethanol, Ether, such as alcohols, such as propanol and butanol,

diethylether, and a tetrahydrofuran, Ketone, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone. The solvent polymerization which uses solution and water, such as acetic acid, chloride, and perchloric acid, for a solvent as independence or multiple mixed liquor or slurry polymerization, a vapor phase polymerization, high voltage ionic polymerization in the inside of a gaseous monomer, etc. are possible, and either a continuation polymerization or a batch process polymerization is possible.

[0033]In a solvent polymerization or slurry polymerization, although the polymerization temperature can usually take the range of -50-200 **, the range of -20-100 ** is preferred especially, and polymerization pressure has ordinary pressure - preferred 60 kg/cm²G. In a vapor phase polymerization, 1 - 30 kg/cm²G of polymerization temperature is [60-120 ** and polymerization pressure] preferred. In high voltage ionic polymerization, 300 - 2500 kg/cm²G of polymerization temperature is [150-300 ** and polymerization pressure] preferred. Although polymerization time is generally suitably determined by the kind of polymer made into the purpose, and the reaction apparatus, it can usually take the range of for [1 minute] - 20 hours. This invention can also add chain transfer agents, such as hydrogen, in order to adjust the molecular weight of a copolymer.

[Translation done.]

EXAMPLE

[Example]Although an example explains this invention concretely, this invention does not have the range hereafter limited by this example. [eta] in an example is the limiting viscosity measured at 135 ** by using a tetralin as a solvent.

[0034]In the 300-ml round-bottom separable flask which carried out the example 1 nitrogen purge, dichlorobis (benzonitrile) palladium 0.001 millimol, 10 ml (50 millimols as norbornene) of toluene solutions of the norbornene of 100 ml of drying toluene and 5-mol [l.] concentration and water 1mmol were taught and warmed, and it made with a 50 ** homogeneous solution. Here, triphenylmethyl tetrakis (pentafluorophenyl) borate 0.001 millimol was added here, and churning was continued for 15 minutes at 50 **. Then, this reaction mixture was invested in 100 ml of methanol, and RO ** of the precipitating white solid was carried out. The yield of the polymer which obtained it with methanol by carrying out reduced pressure drying of this solid after washing was 288 mg (1150 kg/mol-Pd as 6.1% and catalytic activity as an inversion rate of norbornene). The absorption based on a carbon-carbon double bond was not observed in the infrared absorption spectrum of this polymer, but it was confirmed that this polymer is poly norbornene of saturation structure. [eta] of this polymer was 0.63 dl/g.

[0035]Except having changed the water in example 2 Example 1 into 40% glyoxal solution 145mul, it was operated like Example 1 and 1.44 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5760 kg/mol-Pd as catalytic activity 31%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0036]Except having changed the water in example 3 Example 1 into 1.0 mol/l. of chloride 18mul, it was operated like Example 1 and 305 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1220 kg/mol-Pd as catalytic

activity 6.5%. $[\eta]$ of the polymer was 0.28 dl/g.

[0037]Except having changed the water in example 4 Example 1 into 60% perchloric acid solution 160mul, it was operated like Example 1 and 1.84 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 7350 kg/mol-Pd as catalytic activity 39%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0038]Except having changed the water in example 5 Example 1 into 31% hydrogen-peroxide-solution 18mul, it was operated like Example 1 and 338 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1350 kg/mol-Pd as catalytic activity 7.2%. $[\eta]$ of this polymer was 1.23 dl/g.

[0039]Except having changed the water in example 6 Example 1 into 42% hydro acid [dim-ized] solution 209mul, it was operated like Example 1 and 1.447 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5790 kg/mol-Pd as catalytic activity 31%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0040]Except having changed the water in example 7 Example 1 into boric acid, it was operated like Example 1 and 585 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 2320 kg/mol-Pd as catalytic activity 12%. $[\eta]$ of this polymer was 2.38 dl/g.

[0041]Except having changed water 1mmol in example 8 Example 1 into tongue strike IV phosphoric acid hydrate 0.1mmol, it was operated like Example 1 and 1.24 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 4950 kg/mol-Pd as catalytic activity 26%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0042]Except having changed water 1mmol in example 9 Example 1 into tongue strike IV phosphoric acid hydrate 0.1mmol and water 1mmol, it was operated like Example 1 and 1.83 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 7320 kg/mol-Pd as catalytic activity 39%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene.

[0043]Except having changed the water in example 10 Example 1 into 1.0 mol/l. of acetic acid 18mul, it was operated like Example 1 and 1.25 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 4990 kg/mol-Pd as catalytic activity 27%. $[\eta]$ of this polymer was 2.33 dl/g.

[0044]Except having changed the water in example 11 Example 1 into 1.0 mol/l. of formic acid 18mul, it was operated like Example 1 and 0.398 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1590 kg/mol-Pd as catalytic activity 8.5%. $[\eta]$ of this polymer was 2.62 dl/g.

[0045]Except having changed water 1mmol in example 12 Example 1 into triphloroacetic acid 1mmol and water 1mmol, it was operated like Example 1 and 307 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1240 kg/mol-Pd as catalytic activity 6.6%. $[\eta]$ of this polymer was 0.37 dl/g.

[0046]Except having changed the water in example 13 Example 1 into phenol, it was operated like Example 1 and 276 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1100 kg/mol-Pd as catalytic activity 5.9%. $[\eta]$ of this polymer was 0.36 dl/g.

[0047]Except having changed the water in example 14 Example 1 into pentafluorophenol, it was

operated like Example 1 and 175 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 700 kg/mol-Pd as catalytic activity 3.7%.

[0048]Except having changed the water in example 15 Example 1 into 4-methoxyphenol, it was operated like Example 1 and 270 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1080 kg/mol-Pd as catalytic activity 5.7%.

[eta] of this polymer was 0.57 dl/g.

[0049]Except having changed the water in example 16 Example 1 into hydroquinone, it was operated like Example 1 and 436 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1740 kg/mol-Pd as catalytic activity 9.3%.

[0050]Except not having added water 1mmol in comparative example 1 Example 1, when it was operated like Example 1, 150 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 600 kg/mol-Pd as catalytic activity 3.2%. [eta] of this polymer was 0.20 dl/g.

[0051]Except having changed water 1mmol in example 17 Example 1 into water 10mmol, it was operated like Example 1 and 892 mg of poly norbornene was obtained. This yield is equivalent to % as an inversion rate of norbornene, and equivalent to 3570 kg/mol-Pd as catalytic activity.

[eta] of this polymer was 1.92 dl/g.

[0052]Except having changed water 1mmol in example 18 Example 1 into water 50mmol, it was operated like Example 1 and 1.31 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5220 kg/mol-Pd as catalytic activity 28%.

[eta] of this polymer was 2.74 dl/g.

[0053]Except having changed water 1mmol in example 19 Example 1 into water 100mmol, it was operated like Example 1 and 1.28 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5130 kg/mol-Pd as catalytic activity 27%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in toluene. [eta] of the 135 ** tetralin fusible part of this polymer was dl/g.

[0054]Except having changed 100 ml of drying toluene in the example 20 comparative example 1 into 100 ml of water, it was operated like the comparative example 1 and 818 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 3270 kg/mol-Pd as catalytic activity 17%. The system of reaction was presenting the slurry form to which the formed polymer was suspended in water. It was insoluble also to toluene in this polymer.

[0055]Except having changed 1.0 mol/l. of acetic acid 18mul in example 21 Example 10 into 0.01 mol/l. of acetic acid 18mul, it was operated like Example 10 and 712 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 2850 kg/mol-Pd as catalytic activity 15%. [eta] of this polymer was 1.81 dl/g.

[0056]Except having changed 1.0 mol/l. of acetic acid 18mul in example 22 Example 10 into 0.1 mol/l. of acetic acid 18mul, it was operated like Example 10 and 1.382 g of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 5530 kg/mol-Pd as catalytic activity 29%. [eta] of this polymer was 2.79 dl/g.

[0057]Except having changed 1.0 mol/l. of acetic acid 18mul in example 23 Example 10 into 10 mol/l. acetic acid 18mul, it was operated like Example 10 and 902 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 3610 kg/mol-Pd as catalytic activity 19%. [eta] of this polymer was 1.87 dl/g.

[0058]Except having changed churning time 15 minutes in example 24 Example 1 in 60 minutes,

it was operated like Example 1 and 844 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 844 kg/mol-Pd as catalytic activity 18%. [eta] of this polymer was 0.89 dl/g.

[0059]Except having changed churning time 15 minutes in the comparative example 2 comparative example 1 in 60 minutes, it was operated like the comparative example 1 and 350 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 350 kg/mol-Pd as catalytic activity 7.5%. [eta] of this polymer was 0.55 dl/g.

[0060]In the 300-ml round-bottom separable flask which carried out the example 25 nitrogen purge, palladium acetylacetonate 0.002 millimol, 3 ml (30 millimols as norbornene) of toluene solutions of the norbornene of 27 ml of drying toluene and 5-mol [l.] concentration and water 20mmol were taught and warmed, and it made with a 50 ** homogeneous solution. Here, triphenylmethyl tetrakis (pentafluorophenyl) borate 0.002 millimol was added here, and churning was continued for 5 minutes at 50 **. This reaction mixture was invested in 100 ml of methanol, and RO ** of the precipitating white solid was carried out. The yield of the polymer which obtained it with methanol by carrying out reduced pressure drying of this solid after washing was 790 mg (4740 kg/mol-Pd as 56% and catalytic activity as an inversion rate of norbornene). The absorption based on a carbon-carbon double bond was not observed in the infrared absorption spectrum of this polymer, but it was confirmed that this polymer is poly norbornene of saturation structure. [eta] of this polymer was 3.25 dl/g.

[0061]Except not having added water 20mmol in comparative example 3 Example 25, it was operated like Example 25 and 177 mg of poly norbornene was obtained. This yield corresponds as an inversion rate of norbornene, and is equivalent to 1060 kg/mol-Pd as catalytic activity 13%.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is a flow chart figure for helping an understanding of this invention. This flow chart figure is an example of representation of the embodiment of this invention, and this invention is not limited to this at all.

(A) 遷移金属成分

遷移金属化合物

(B) 有機金属成分

(C) 第三成分

遷移金属化合物と反応して
イオン性の錯体を形成する化合物

水または酸

環状オレフィン

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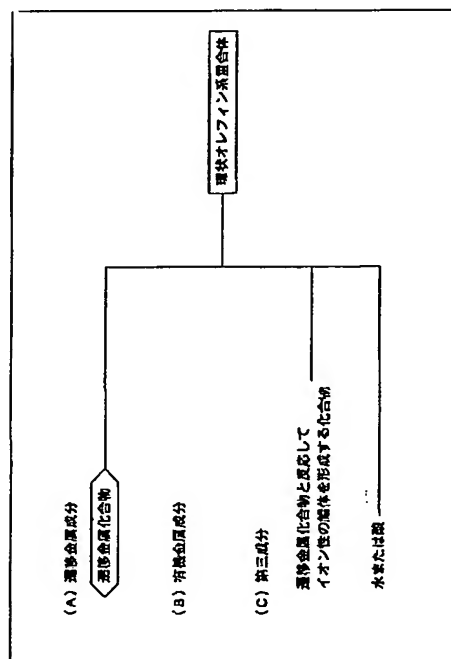
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(54) 【発明の名称】 環状オレフィン類重合用触媒及び環状オレフィン系重合体の製造方法

(57) 【要約】

【課題】 極めて少量の触媒で高い環状オレフィン類の転化率を実現する環状オレフィン類重合用触媒、および高分子量の環状オレフィン系重合体を製造する方法を提供する。

【解決手段】 (A) 遷移金属化合物、(B) 遷移金属化合物と反応してイオン性の錯体を形成する化合物、及び (C) 水または酸を含有する環状オレフィン類重合用触媒、並びに該触媒を用いて環状オレフィン類を重合する環状オレフィン系重合体の製造方法。(A) 遷移金属化合物、および (B) 遷移金属化合物と反応してイオン性の錯体を形成する化合物を含有する触媒を用いて、水を分散溶媒として、環状オレフィン類を重合する環状オレフィン系重合体の製造方法。



【特許請求の範囲】

【請求項1】(A)遷移金属化合物、(B)遷移金属化合物と反応してイオン性の錯体を形成する化合物、及び(C)水を含有することを特徴とする環状オレフィン類重合用触媒。

【請求項2】(A)遷移金属化合物、(B)遷移金属化合物と反応してイオン性の錯体を形成する化合物、及び(C)酸を含有することを特徴とする環状オレフィン類重合用触媒。

【請求項3】酸(C)が、ブレンステッド酸であることを特徴とする請求項2記載の環状オレフィン類重合用触媒。

【請求項4】ブレンステッド酸が、無機酸であることを特徴とする請求項3記載の環状オレフィン類重合用触媒。

【請求項5】ブレンステッド酸が、ヘテロポリ酸またはその水和物であることを特徴とする請求項3記載の環状オレフィン類重合用触媒。

【請求項6】ブレンステッド酸が、カルボン酸化合物であることを特徴とする請求項3記載の環状オレフィン類重合用触媒。

【請求項7】ブレンステッド酸が、フェノールもしくはフェノール類であることを特徴とする請求項3記載の環状オレフィン類重合用触媒。

【請求項8】遷移金属化合物(A)が第10族遷移金属化合物であることを特徴とする請求項1～7のいずれかに記載の環状オレフィン類重合用触媒。

【請求項9】遷移金属化合物(A)がパラジウム化合物であることを特徴とする請求項1～7のいずれかに記載の環状オレフィン類重合用触媒。

【請求項10】遷移金属化合物と反応してイオン性の錯体を形成する化合物(B)が、遷移金属化合物との反応により非配位性のアニオンを生成する化合物であることを特徴とする請求項1～9のいずれかに記載の環状オレフィン類重合用触媒。

【請求項11】遷移金属化合物と反応してイオン性の錯体を形成する化合物(B)が、下記(B1)～(B3)のいずれかであることを特徴とする請求項1～9のいずれかに記載の環状オレフィン類重合用触媒。

(B1)一般式 $BQ^1Q^2Q^3$ で表されるホウ素化合物

(B2)一般式 $G^+(BQ^1Q^2Q^3Q^4)^-$ で表されるホウ素化合物

(B3)一般式 $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$ で表されるホウ素化合物

(式中、Bは3価の原子価状態のホウ素原子であり、 $Q^1 \sim Q^4$ はハロゲン原子、1～20個の炭素原子を含む炭化水素基、1～20個の炭素原子を含むハロゲン化炭化水素基、1～20個の炭素原子を含む置換シリル基、1～20個の炭素原子を含むアルコキシ基または2～40個の炭素原子を含む2置換アミノ基であり、それらは

同じであっても異なっても良い。 G^+ は遷移金属を酸化してカチオンにすることができるカチオン性酸化剤、あるいは遷移金属化合物から配位子を引き抜くことのできるカチオンである。Lは中性ルイス塩基であり、 $(L-H)^+$ はブレンステッド酸である。)

【請求項12】請求項1～11のいずれかに記載の触媒を用いて環状オレフィン類を重合することを特徴とする環状オレフィン系重合体の製造方法。

【請求項13】(A)遷移金属化合物、および(B)遷移金属化合物と反応してイオン性の錯体を形成する化合物を含有する触媒を用いて、水を分散溶媒として、環状オレフィン類を重合することを特徴とする環状オレフィン系重合体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は環状オレフィン類重合用触媒および環状オレフィン系重合体の製造方法に関する。

【0002】

【従来の技術】ノルボルネンに代表される環状オレフィン類は各種の重合法によって重合し、付加構造を主体とする環状オレフィン系重合体を与えることが知られている。このような環状オレフィン系重合体は、一般に、非環状のオレフィン系重合体に比して高いガラス転移温度を有しており、高耐熱性樹脂としてフィルムや各種成形品としての応用が期待されている。

【0003】かかる環状オレフィン系重合体の製造法としては各種のものが知られている。例えばノルボルネン系重合体については、米国特許第3330815号明細書に $Pd(C_6H_5CN)_2Cl_2$ を触媒に用いる方法が提案されており、また特開平4-63807号公報には遷移金属化合物成分とアルミノキサン成分とからなる触媒を用いる方法が提案されている。しかし、前者には触媒活性が低いという問題があり、後者には多量のアルミノキサンを用いなければならないために重合体中に多量の金属が残留し、重合体の劣化や着色等の原因になるという問題があった。

【0004】特開平5-262821号公報には遷移金属化合物成分および遷移金属化合物と反応してイオン性の錯体を形成する化合物成分とからなる触媒を用いて、共重合体を含む環状オレフィン系重合体を製造する方法が提案されている。該方法はアルミノキサン等の助触媒を多量に用いることなく比較的高い触媒効率を達成できるという点で優れた方法であるが、環状オレフィン類の転化率が低いという点、および多くの場合助触媒として取り扱いの難しい有機アルミニウム化合物の使用を必要とする点でまだ十分ではない。

【0005】かかる問題点が改善された方法として、特開平7-304834号公報にはパラジウム化合物及び遷移金属化合物と反応してイオン性の錯体を形成する化

化合物を主成分とする触媒を用いた環状オレフィン系重合体の製造方法が提案されている。該方法は環状オレフィン類を高い転化率で重合し得る方法として優れたものであるが、工業的にはさらに高い触媒活性、及び得られるポリマーの分子量の向上が望まれていた。

【0006】一方、遷移金属化合物を用いた環状オレフィン類の重合系に水を添加する研究はこれまでも行われており、例えば、Macromol. Symp. 89, 433 (1995) では、 $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4][\text{BF}_4]_2$ を触媒とするノルボルネンの重合において、水を添加しても重合体が得られることが証明されているが、重合活性及び得られる重合体の分子量は無添加系に比べ共に低下している。このように、環状オレフィン系重合体については、現在のところまだ工業的に満足な方法は見つかっていないというのが実状である。

【0007】

【発明が解決しようとする課題】本発明は上記事情に鑑みてなされたものである。即ち、本発明の課題は、極めて少量の触媒で高い環状オレフィン類の転化率を実現する環状オレフィン類重合用触媒、および高分子量の環状オレフィン系重合体を製造する方法を提供することにある。

【0008】

【課題を解決するための手段】本発明者らは上記課題を解決すべく鋭意検討を重ねた結果、特定の触媒系にさらに水または酸を一成分として加えた触媒を見出し本発明

を完成するに至った。即ち本発明は、(A) 遷移金属化合物、(B) 遷移金属化合物と反応してイオン性の錯体を形成する化合物、及び(C) 水または酸を含有する環状オレフィン類重合用触媒、並びに該触媒を用いて環状オレフィン類を重合する環状オレフィン系重合体の製造方法にかかるものである。さらに本発明は、(A) 遷移金属化合物、および(B) 遷移金属化合物と反応してイオン性の錯体を形成する化合物を含有する触媒を用いて、水を分散溶媒として、環状オレフィン類を重合する環状オレフィン系重合体の製造方法にかかるものである。

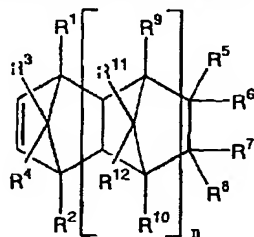
【0009】

【発明の実施の形態】以下、本発明を詳細に説明する。

(1) 環状オレフィン類

本発明において使用される環状オレフィン類とは各種の置換基を有してもよい4個以上の炭素原子が環を形成し、該環の中に1個の炭素-炭素二重結合を含む化合物のことである。このような環状オレフィン類としてはシクロブテン、シクロペンテン、シクロヘキセン等の単環状オレフィン；3-メチルシクロペンテン、3-メチルシクロヘキセン等の置換単環状オレフィン；ノルボルネンや1, 2-ジヒドロジシクロペンタジエン等の多環状オレフィン；1-メチルノルボルネンや5-メチルノルボルネン等の置換多環状オレフィンが例示される。

【0010】これらの中で好ましい環状オレフィン類は、下記一般式〔I〕で表わされる化合物である。



〔I〕

(式中、 $\text{R}^1 \sim \text{R}^{12}$ はそれぞれ独立に水素原子、ハロゲン原子、水酸基、アミノ基および炭素原子数1～20の有機基からなる群から選ばれる置換基を示し、 R^5 、 R^6 と R^7 、 R^8 は環を形成してもよい。 n は0以上の整数を示す。)

【0011】ここに置換基の一員である炭素原子数1～20の有機基の具体例としてはメチル基、エチル基、プロピル基、ブチル基、ヘキシル基、オクチル基、ドデシル基等のアルキル基；フェニル基、トリル基、ナフチル基等のアリール基；ベンジル基、フェネチル基等のアラルキル基；メチリデン基、エチリデン基等のアルキリデン基；ビニル基、アリル基等のアルケニル基；メトキシ基、エトキシ基等のアルコキシ基；フェノキシ基等のアリーロキシ基；アセチル基等のアシル基；メトキシカルボニル基、エトキシカルボニル基等のアルコキシカルボニル基；アセチルオキシ基等のアシルオキシ基；トリメ

チルシリル基等の(置換)シリル基；ジメチルアミノ基、ジエチルアミノ基等のアルキルアミノ基；カルボキシ基；シアノ基；並びに上記アルキル基、アリール基およびアラルキル基の水素原子の一部がハロゲン原子、水酸基、アミノ基、アシル基、カルボキシ基、アルコキシ基、アルコキシカルボニル基、アシルオキシ基、(置換)シリル基、アルキルアミノ基あるいはシアノ基で置換された基を挙げることができる。

【0012】好ましい置換基は、水素原子、炭素原子数1～20のアルキル基、炭素原子数6～20のアリール基、炭素原子数7～20のアラルキル基、炭素原子数1～20のアルキリデン基、炭素原子数2～20のアルケニル基、炭素原子数1～20のアシル基、炭素原子数1～20のアルコキシカルボニル基、炭素原子数1～20のアシルオキシ基、炭素原子数1～20の(置換)シリル基である。

【0013】一般式〔I〕で表される好ましい環状オレフィン類の具体例としては、ノルボルネン、5-メチルノルボルネン、5-エチルノルボルネン、5-ブチルノルボルネン、5-フェニルノルボルネン、5-ベンジルノルボルネン、テトラシクロドデセン、トリシクロドセン、トリシクロウンデセン、ペンタシクロペンタデセン、ペンタシクロヘキサデセン、エチリデンノルボルネン、8-メチルテトラシクロドデセン、8-エチルテトラシクロドデセン、5-アセチルノルボルネン、5-アセチルオキシノルボルネン、5-メトキシカルボニルノルボルネン、5-エトキシカルボニルノルボルネン、5-メチル-5-メトキシカルボニルノルボルネン、5-シアノノルボルネン、8-メトキシカルボニルテトラシクロドデセン、8-メチル-8-メトキシカルボニルテトラシクロドデセン、8-シアノテトラシクロドデセン等を列挙することができる。

【0014】重合に際してこれらの環状オレフィン類は単独または複数で使用される。また、環状オレフィン系重合体の有する優れた性質を損なわない範囲、すなわち一般には全単量体中の環状オレフィン類の割合が10重量%を下回らない範囲、好ましくは50重量%を下回らない範囲で、環状オレフィン類と共重合性のある他の単量体を、環状オレフィン類と一緒に用いることは何ら差し支えない。かかる他の単量体の例としてはエチレン、プロピレン、1-ブテン、4-メチルペンテン-1、1-ヘキセン、1-オクテン等の α -オレフィン；スチレン等のアルケニル芳香族炭化水素；メチルビニルエーテル、エチルビニルエーテル等のアルキルビニルエーテル；塩化ビニル等の不飽和ハロゲン化炭化水素；メチルアクリレート、エチルアクリレート、メチルメタクリレート等の α 、 β -不飽和カルボン酸エステル；アクリロニトリル等の不飽和ニトリル；酢酸ビニル等のカルボン酸ビニル等を挙げることができる。

【0015】(2) 遷移金属化合物(A)

本発明の触媒における(A)成分は、遷移金属化合物である。ここで遷移金属化合物とは、周期律表(IUPAC無機化学命名法改訂版、1989)の第6族から第11族の元素を有する化合物のことである。かかる第6族から第11族の元素の具体例としては、クロム、モリブデン、タングステン、マンガン、鉄、ルテニウム、コバルト、ロジウム、ニッケル、パラジウム、白金、銅、銀等が挙げられる。これらの元素を有する化合物であれば特に限定されるものではないが、好ましい遷移金属化合物は、第10族遷移金属化合物であり、ニッケル、パラジウム、白金などの各種化合物である。

【0016】その具体例としては、塩化ニッケル、硫酸ニッケル、過塩素酸ニッケル等のニッケルの無機酸塩；酢酸ニッケル、蔞酸ニッケル等のニッケルの有機酸塩；ニッケルアセチルアセトネート、ニッケルフタロシアニン等のニッケル錯体；塩化パラジウム、臭化パラジ

ウム、ヨウ化パラジウム、硫酸パラジウム、硝酸パラジウム等のパラジウムの無機酸塩；酢酸パラジウム、トリフルオロ酢酸パラジウム、シアン化パラジウム等のパラジウムの有機酸塩；パラジウムアセチルアセトネート、ビス(アリル)パラジウム、ジクロロ(1, 5-シクロオクタジエン)パラジウム、ジクロロビス(アセトニトリル)パラジウム、ジクロロビス(ベンゾニトリル)パラジウム、カルボニルトリス(トリフェニルホスフィン)パラジウム、ジクロロビス(トリエチルホスフィン)パラジウム、ジアセトビス(トリフェニルホスフィン)パラジウム、テトラキス(トリフェニルホスフィン)パラジウム、ジクロロ[1, 2-ビス(ジフェニルホスフィノ)エタン]パラジウム、ビス[1, 2-ビス(ジフェニルホスフィノ)エタン]パラジウム、テトラアミンパラジウムナイトレート、テトラキス(アセトニトリル)パラジウムテトラフルオロボレート等のパラジウム錯体；塩化白金、ヨウ化白金等の白金の無機酸塩；白金アセチルアセトネート等の白金錯体等を挙げることができる。これらの中で好ましい第10族遷移金属化合物はパラジウムの化合物とニッケルの化合物であり、さらに好ましい第10族遷移金属化合物はパラジウムの化合物である。特に好ましい遷移金属化合物(A)は、塩化パラジウム、臭化パラジウム、ヨウ化パラジウム、硫酸パラジウム、硝酸パラジウム、酢酸パラジウム、ジクロロビス(アセトニトリル)パラジウム、ジクロロビス(ベンゾニトリル)パラジウム、及びパラジウムアセチルアセトネートである。

【0017】(3) 遷移金属化合物と反応してイオン性の錯体を形成する化合物(B)

本発明の触媒における(B)成分は、遷移金属化合物と反応してイオン性の錯体を形成する化合物である。遷移金属化合物と反応してイオン性の錯体を形成する化合物(B)は、遷移金属化合物と反応してイオン性の錯体を形成しうるものであれば、いずれのものでも使用できる。好ましくは化合物(B)は、遷移金属化合物との反応により非配位性のアニオンを生成する化合物である。

【0018】好ましくは、(B1) 遷移金属化合物をカチオンに対応する非配位性アニオンになることができるルイス酸、(B2) 一般式 $G^+ A^-$ (但し、 G^+ は遷移金属を酸化してカチオンにすることができるカチオン性酸化剤、あるいは遷移金属化合物から配位子を引き抜くことのできるカチオンであり、 A^- は非配位性アニオンである。) で表される化合物、もしくは(B3) 一般式 $(L-H)^+ A^-$ (但し、 L は中性ルイス塩基であり、 $(L-H)^+$ はブレンステッド酸であり、遷移金属をカチオンにすることができ、そして A^- は非配位性アニオンである。) で表される化合物のいずれかである。

【0019】より好ましくは、(B1)、(B2)、(B3) はそれぞれホウ素化合物である。

【0020】上記のルイス酸(B1)は、さらに好まし

くは、一般式 $BQ^1 Q^2 Q^3$ で表されるホウ素化合物である。但し、Bは3価の原子価状態のホウ素原子であり、 $Q^1 \sim Q^3$ はハロゲン原子、1~20個の炭素原子を含む炭化水素基、1~20個の炭素原子を含むハロゲン化炭化水素基、1~20個の炭素原子を含む置換シリル基、1~20個の炭素原子を含むアルコキシ基または2~40個の炭素原子を含む2置換アミノ基であり、それらは同じであっても異なっても良い。

【0021】ルイス酸(B1)の具体例としては、トリス(ペンタフルオロフェニル)ボラン、トリス(2, 3, 5, 6-テトラフルオロフェニル)ボラン、トリス(2, 3, 4, 5-テトラフルオロフェニル)ボラン、トリス(3, 4, 5-トリフルオロフェニル)ボラン、トリス(2, 3, 4-トリフルオロフェニル)ボラン、フェニルビス(ペンタフルオロフェニル)ボラン等が挙げられるが、最も好ましくは、トリス(ペンタフルオロフェニル)ボランである。

【0022】上記の一般式 $G^+ A^-$ で表される化合物(B2)は、さらに好ましくは、一般式 $G^+ (BQ^1 Q^2 Q^3 Q^4)^-$ で表されるホウ素化合物である。但し、Bは3価の原子価状態のホウ素原子であり、 $Q^1 \sim Q^4$ は上記のルイス酸(B1)における $Q^1 \sim Q^3$ と同様である。

【0023】一般式 $G^+ (BQ^1 Q^2 Q^3 Q^4)^-$ で表される化合物の具体例としては、カチオン性酸化剤である G^+ には、フェロセニウムカチオン、アルキル置換フェロセニウムカチオン、銀陽イオンなどが挙げられ、遷移金属化合物から配位子を引き抜くことのできるカチオンである G^+ には、トリフェニルメチルカチオンなどが挙げられる。非配位性アニオンである $(BQ^1 Q^2 Q^3 Q^4)^-$ には、テトラキス(ペンタフルオロフェニル)ボレート、テトラキス(2, 3, 5, 6-テトラフルオロフェニル)ボレート、テトラキス(2, 3, 4, 5-テトラフルオロフェニル)ボレート、テトラキス(3, 4, 5-トリフルオロフェニル)ボレート、テトラキス(2, 2, 4-トリフルオロフェニル)ボレート、フェニルビス(ペンタフルオロフェニル)ボレート、テトラキス(3, 5-ビストリフルオロメチルフェニル)ボレートなどが挙げられる。

【0024】これらの具体的な組み合わせとしては、フェロセニウムテトラキス(ペンタフルオロフェニル)ボレート、1, 1'-ジメチルフェロセニウムテトラキス(ペンタフルオロフェニル)ボレート、銀テトラキス(ペンタフルオロフェニル)ボレート、トリフェニルメチルテトラキス(ペンタフルオロフェニル)ボレート、トリフェニルメチルテトラキス(3, 5-ビストリフルオロメチルフェニル)ボレートなどを挙げることができるが、最も好ましくは、トリフェニルメチルテトラキス(ペンタフルオロフェニル)ボレートである。

【0025】また、上記の一般式 $(L-H)^+ A^-$ で表

される化合物(B3)は、さらに好ましくは、一般式 $(L-H)^+ (BQ^1 Q^2 Q^3 Q^4)^-$ で表されるホウ素化合物である。但し、Bは3価の原子価状態のホウ素原子であり、 $Q^1 \sim Q^4$ は上記のルイス酸(B1)における $Q^1 \sim Q^3$ と同様である。

【0026】一般式 $(L-H)^+ (BQ^1 Q^2 Q^3 Q^4)^-$ で表される化合物の具体例としては、ブレンステッド酸である $(L-H)^+$ には、トリアルキル置換アンモニウム、N, N-ジアルキルアニリニウム、ジアルキルアンモニウム、トリアリールホスホニウムなどが挙げられ、非配位性アニオンである $(BQ^1 Q^2 Q^3 Q^4)^-$ には、前述と同様のものが挙げられる。

【0027】これらの具体的な組み合わせとしては、トリエチルアンモニウムテトラキス(ペンタフルオロフェニル)ボレート、トリプロピルアンモニウムテトラキス(ペンタフルオロフェニル)ボレート、トリ(ノルマルブチル)アンモニウムテトラキス(ペンタフルオロフェニル)ボレート、トリ(ノルマルブチル)アンモニウムテトラキス(3, 5-ビストリフルオロメチルフェニル)ボレート、N, N-ジメチルアニリニウムテトラキス(ペンタフルオロフェニル)ボレート、N, N-ジエチルアニリニウムテトラキス(ペンタフルオロフェニル)ボレート、N, N-2, 4, 6-ペンタメチルアニリニウムテトラキス(ペンタフルオロフェニル)ボレート、N, N-ジメチルアニリニウムテトラキス(3, 5-ビストリフルオロメチルフェニル)ボレート、ジイソプロピルアンモニウムテトラキス(ペンタフルオロフェニル)ボレート、ジシクロヘキシルアンモニウムテトラキス(ペンタフルオロフェニル)ボレート、トリフェニルホスホニウムテトラキス(ペンタフルオロフェニル)ボレート、トリ(メチルフェニル)ホスホニウムテトラキス(ペンタフルオロフェニル)ボレート、トリ(ジメチルフェニル)ホスホニウムテトラキス(ペンタフルオロフェニル)ボレートなどを挙げることができるが、最も好ましくは、トリ(ノルマルブチル)アンモニウムテトラキス(ペンタフルオロフェニル)ボレート、もしくは、N, N-ジメチルアニリニウムテトラキス(ペンタフルオロフェニル)ボレートである。

【0028】(4)水または酸(C)

本発明の触媒における(C)成分は、水または酸である。酸として好ましくはブレンステッド酸である。ここでブレンステッド酸とは、プロトンを与える性質を有する化合物のことであり、そのような性質を有する化合物であれば、特に限定されるものではない。酸の具体例としては、塩酸、硫酸、硝酸、次亜塩素酸、過塩素酸、硼酸、磷酸、過マンガン酸、重クロム酸、過酸化水素水、ほうふつ化水素酸等の無機酸；タングストリン酸、モリブドリン酸等のヘテロポリ酸またはその水和物；ギ酸、酢酸、プロピオン酸、トリフロロ酢酸、モノクロロ酢酸、ジクロロ酢酸、酪酸、安息香酸、メチル安息香酸、

クロロ安息香酸、メトキシ安息香酸、フマル酸、マレイン酸、サルチル酸、ナフタリンカルボン酸等のカルボン酸類；フェノール、クレゾール、フロロフェノール、クロロフェノール、ヒドロキノン、ブロモフェノール、メトキシフェノール、シアノフェノール、アミノフェノール、ニトロフェノール、ペンタフロロフェノール等のフェノール類；シリカやアルミナ等の固体酸が挙げられる。

【0029】好ましいプレnstेटド酸は、塩酸、過塩素酸、硼酸、過酸化水素水、タングストリン酸、ほうふっ化水素酸、ギ酸、酢酸、プロピオン酸、トリフロロ酢酸、安息香酸、フマル酸、マレイン酸、グリオキサール、フェノール、ペンタフロロフェノール、4-メトキシフェノール、クレゾール、ヒドロキノンである。これらの化合物は単独または複数で使用することができる。

【0030】(5) 環状オレフィン類重合用触媒
本発明の環状オレフィン類重合用触媒は、上記(A)成分、(B)成分、及び(C)成分を含有する触媒である。これらの成分は、例えば、適当な溶媒中で(A)成分、(B)成分及び(C)成分を予め混合した溶液として用いてもよいし、重合系へ(A)成分、(B)成分及び(C)成分、あるいはそれらをモノマーまたは適当な溶媒に溶かした溶液を同時または別々に供給して重合系内で接触させてもよい。

【0031】成分(A)の使用量は選ばれる環状オレフィン類の種類や他の重合条件によってその好適な値が異なるため、一概にその範囲を定めることはできないが、通常、使用されるモノマーに対して0.0001~1モル%、好ましくは0.0001~0.1モル%である。成分(B)の使用量も特に制限されないが、成分(A)1モル当たり、通常0.1~100モル、好ましくは0.5~10モルである。成分(C)の使用量もまた、制限されることはないが、通常成分(A)1モル当たり、0.001モル以上である。好ましくは成分(A)1モル当たり、0.1~100000モル程度であるが、大量に使用して重合溶媒として用いることも可能である。

【0032】(6) 環状オレフィン系重合体の製造
本発明において、重合方法は特に限定されるべきものではないが、例えば、ブタン、ペンタン、ヘキサン、ヘプタン、オクタン等の脂肪族炭化水素、ベンゼン、トルエン、キシレン等の芳香族炭化水素、メチレンジクロライド、エチレンジクロライド等のハロゲン化炭化水素、メタノール、エタノール、プロパノール、ブタノール等のアルコール類、ジエチルエーテル、テトラヒドロフラン等のエーテル、アセトン、メチルエチルケトン、メチルイソブチルケトン等のケトン類の他、酢酸、塩酸、過塩素酸等の水溶液及び水を単独、あるいは複数の混合液として溶媒に用いる溶媒重合、又はスラリー重合、ガス状のモノマー中での気相重合や高圧イオン重合等が可能で

あり、また、連続重合、回分式重合のどちらでも可能である。

【0033】溶媒重合やスラリー重合において、重合温度は通常-50~200℃の範囲を取り得るが、特に、-20~100℃の範囲が好ましく、重合圧力は、常圧~60kg/cm² Gが好ましい。気相重合においては、重合温度は60~120℃、重合圧力は1~30kg/cm² Gが好ましい。高圧イオン重合では、重合温度は150~300℃、重合圧力は300~2500kg/cm² Gが好ましい。重合時間は、一般的に、目的とするポリマーの種類、反応装置により適宜決定されるが、通常1分間~20時間の範囲を取ることができる。また、本発明は共重合体の分子量を調節するために水素等の連鎖移動剤を添加することもできる。

【実施例】以下、実施例により本発明を具体的に説明するが、本発明はかかる実施例によりその範囲を限定されるものではない。なお、実施例中における[η]とは、テトラリンを溶媒として135℃で測定した極限粘度のことである。

【0034】実施例1

窒素置換した300mlの丸底セバブルフラスコ中にジクロロビス(ベンゾニトリル)パラジウム0.001ミリモル、脱水トルエン100ml、5モル/リットル濃度のノルボルネンのトルエン溶液10ml(ノルボルネンとして50ミリモル)、水1mmolを仕込み、加熱して50℃の均一溶液となした。ここへ、トリフェニルメチルテトラキス(ペンタフルオロフェニル)ボレート0.001ミリモルを加え、50℃で15分間攪拌を続けた。その後、該反応液をメタノール100mlに投じ、沈殿した白色固体をろ取した。該固体をメタノールで洗浄後、減圧乾燥して得た重合体の収量は288mg(ノルボルネンの転化率として6.1%、触媒活性として1150kg/mol-Pd)であった。該重合体の赤外吸収スペクトルには炭素-炭素二重結合に基づく吸収が認められず、該重合体が飽和構造のポリノルボルネンであることが確かめられた。また、該重合体の[η]は0.63dl/gであった。

【0035】実施例2

実施例1における水を40%グリオキサール水溶液145μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.44gを得た。この収量はノルボルネンの転化率として31%、触媒活性として5760kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。

【0036】実施例3

実施例1における水を1.0モル/リットルの塩酸18μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン305mgを得た。この収量はノルボルネンの転化率として6.5%、触媒活性として1220kg/mol-Pdに相当する。また、重合体の[η]は0.

28dl/gであった。

【0037】実施例4

実施例1における水を60%過塩素酸水溶液160μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.84gを得た。この収量はノルボルネンの転化率として39%、触媒活性として7350kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。

【0038】実施例5

実施例1における水を31%過酸化水素水18μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン338mgを得た。この収量はノルボルネンの転化率として7.2%、触媒活性として1350kg/mol-Pdに相当する。また、該重合体の[η]は1.23dl/gであった。

【0039】実施例6

実施例1における水を42%ほうふっ化水素酸水溶液209μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.447gを得た。この収量はノルボルネンの転化率として31%、触媒活性として5790kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。

【0040】実施例7

実施例1における水を硼酸に変えた以外は実施例1と同様に操作し、ポリノルボルネン585mgを得た。この収量はノルボルネンの転化率として12%、触媒活性として2320kg/mol-Pdに相当する。また、該重合体の[η]は2.38dl/gであった。

【0041】実施例8

実施例1における水1mmolを、タングストIVりん酸水和物0.1mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.24gを得た。この収量はノルボルネンの転化率として26%、触媒活性として4950kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。

【0042】実施例9

実施例1における水1mmolを、タングストIVりん酸水和物0.1mmol及び水1mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.83gを得た。この収量はノルボルネンの転化率として39%、触媒活性として7320kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。

【0043】実施例10

実施例1における水を1.0モル/リットルの酢酸18μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.25gを得た。この収量はノルボルネンの転化率として27%、触媒活性として4990kg/mol-Pdに相当する。また、該重合体の[η]は2.33dl/gであった。

【0044】実施例11

実施例1における水を1.0モル/リットルのギ酸18μlに変えた以外は実施例1と同様に操作し、ポリノルボルネン0.398gを得た。この収量はノルボルネンの転化率として8.5%、触媒活性として1590kg/mol-Pdに相当する。また、該重合体の[η]は2.62dl/gであった。

【0045】実施例12

実施例1における水1mmolを、トリフロロ酢酸1mmol及び水1mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン307mgを得た。この収量はノルボルネンの転化率として6.6%、触媒活性として1240kg/mol-Pdに相当する。また、該重合体の[η]は0.37dl/gであった。

【0046】実施例13

実施例1における水をフェノールに変えた以外は実施例1と同様に操作し、ポリノルボルネン276mgを得た。この収量はノルボルネンの転化率として5.9%、触媒活性として1100kg/mol-Pdに相当する。また、該重合体の[η]は0.36dl/gであった。

【0047】実施例14

実施例1における水をペンタフロロフェノールに変えた以外は実施例1と同様に操作し、ポリノルボルネン175mgを得た。この収量はノルボルネンの転化率として3.7%、触媒活性として700kg/mol-Pdに相当する。

【0048】実施例15

実施例1における水を4-メトキシフェノールに変えた以外は実施例1と同様に操作し、ポリノルボルネン270mgを得た。この収量はノルボルネンの転化率として5.7%、触媒活性として1080kg/mol-Pdに相当する。また、該重合体の[η]は0.57dl/gであった。

【0049】実施例16

実施例1における水をヒドロキノンに変えた以外は実施例1と同様に操作し、ポリノルボルネン436mgを得た。この収量はノルボルネンの転化率として9.3%、触媒活性として1740kg/mol-Pdに相当する。

【0050】比較例1

実施例1において水1mmolを加えなかった以外は実施例1と同様に操作したところ、ポリノルボルネン150mgを得た。この収量はノルボルネンの転化率として3.2%、触媒活性として600kg/mol-Pdに相当する。また、該重合体の[η]は0.20dl/gであった。

【0051】実施例17

実施例1における水1mmolを水10mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン8

92mgを得た。この収量はノルボルネンの転化率として%、触媒活性として3570kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は1.92dl/gであった。

【0052】実施例18

実施例1における水1mmolを水50mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.31gを得た。この収量はノルボルネンの転化率として28%、触媒活性として5220kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は2.74dl/gであった。

【0053】実施例19

実施例1における水1mmolを水100mmolに変えた以外は実施例1と同様に操作し、ポリノルボルネン1.28gを得た。この収量はノルボルネンの転化率として27%、触媒活性として5130kg/mol-Pdに相当する。反応系は生成重合体がトルエンに懸濁したスラリー状を呈していた。該重合体の135℃テトラリン可溶部の $[\eta]$ はdl/gであった。

【0054】実施例20

比較例1における脱水トルエン100mlを水100mlに変えた以外は比較例1と同様に操作し、ポリノルボルネン818mgを得た。この収量はノルボルネンの転化率として17%、触媒活性として3270kg/mol-Pdに相当する。反応系は生成重合体が水に懸濁したスラリー状を呈していた。該重合体はトルエンにも不溶であった。

【0055】実施例21

実施例10における1.0mol/リットルの酢酸18 μ lを0.01mol/リットルの酢酸18 μ lに変えた以外は実施例10と同様に操作し、ポリノルボルネン712mgを得た。この収量はノルボルネンの転化率として15%、触媒活性として2850kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は1.81dl/gであった。

【0056】実施例22

実施例10における1.0mol/リットルの酢酸18 μ lを0.1mol/リットルの酢酸18 μ lに変えた以外は実施例10と同様に操作し、ポリノルボルネン1.382gを得た。この収量はノルボルネンの転化率として29%、触媒活性として5530kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は2.79dl/gであった。

【0057】実施例23

実施例10における1.0mol/リットルの酢酸18 μ lを10mol/リットルの酢酸18 μ lに変えた以外は実施例10と同様に操作し、ポリノルボルネン902mgを得た。この収量はノルボルネンの転化率として19%、触媒活性として3610kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は1.87dl/gであ

った。

【0058】実施例24

実施例1における攪拌時間15分を60分に変えた以外は実施例1と同様に操作し、ポリノルボルネン844mgを得た。この収量はノルボルネンの転化率として18%、触媒活性として844kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は0.89dl/gであった。

【0059】比較例2

比較例1における攪拌時間15分を60分に変えた以外は比較例1と同様に操作し、ポリノルボルネン350mgを得た。この収量はノルボルネンの転化率として7.5%、触媒活性として350kg/mol-Pdに相当する。また、該重合体の $[\eta]$ は0.55dl/gであった。

【0060】実施例25

窒素置換した300mlの丸底セパラブルフラスコ中にパラジウムアセチルアセトネート0.002ミリモル、脱水トルエン27ml、5mol/リットル濃度のノルボルネンのトルエン溶液3ml（ノルボルネンとして30ミリモル）、水20mmolを仕込み、加温して50℃の均一溶液となした。ここへ、トリフェニルメチルテトラキス（ペンタフルオロフェニル）ボレート0.002ミリモルを加え、50℃で5分間攪拌を続けた。該反応液をメタノール100mlに投じ、沈殿した白色固体を口取した。該固体をメタノールで洗浄後、減圧乾燥して得た重合体の収量は790mg（ノルボルネンの転化率として56%、触媒活性として4740kg/mol-Pd）であった。該重合体の赤外吸収スペクトルには炭素-炭素二重結合に基づく吸収が認められず、該重合体が飽和構造のポリノルボルネンであることが確かめられた。また、該重合体の $[\eta]$ は3.25dl/gであった。

【0061】比較例3

実施例25において水20mmolを加えなかった以外は実施例25と同様に操作し、ポリノルボルネン177mgを得た。この収量はノルボルネンの転化率として13%、触媒活性として1060kg/mol-Pdに相当する。

【0062】

【発明の効果】以上詳述したように、本発明の方法によれば有用な環状オレフィン系重合体を極めて少量の触媒を用いて効率的に生産できるのであり、その工業的価値は頗る大である。

【図面の簡単な説明】

【図1】図1は本発明の理解を助けるためのフローチャート図である。本フローチャート図は、本発明の実施態様の代表例であり、本発明は、何らこれに限定されるものではない。

【図1】

